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PCT

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>3</sup> :</b> C07D307/18, 309/08, 319/12 C07C 43/12, 41/22; F25B 29/00 F23K 28/00; C10M 3/00	A1	<b>(11) International Publication Number:</b> WO 84/ 02909 <b>(43) International Publication Date:</b> 2 August 1984 (02.08.84)
<b>(21) International Application Number:</b> PCT/GB84/00013 <b>(22) International Filing Date:</b> 20 January 1984 (20.01.84) <b>(31) Priority Application Number:</b> 8301506 <b>(32) Priority Date:</b> 20 January 1983 (20.01.83) <b>(33) Priority Country:</b> GB  <b>(71) Applicants (for JP only):</b> THE ELECTRICITY COUNCIL [GB/GB]; 30 Millbank, London SW1P 4RD (GB). IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Millbank, London SW1P 3JF (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> DRAKESMITH, Frederick, Gerald [GB/GB]; 5 Ffordd Argoed, Bryn Awelon, Mold, Clwyd, Wales (GB). POWELL, Richard, Llewellyn [GB/GB]; 47 The Loont, Winsford, Cheshire CW7 1EX (GB). CHAMBERS, Richard, Dickinson [GB/GB]; 5 Aykley Green, Whitesmocks, Durham DH1 4LN (GB). GRIEVSON, Brian [GB/GB]; Ivy Cottage, Walldridge Hall Farm, Walldridge Colliery, Co. Durham (GB).		<b>(74) Agent:</b> ALLARD, Susan, Joyce; Boulton, Wade & Tennant, 27 Fumival Street, London EC4A 1PQ (GB).  <b>(81) Designated States:</b> JP, US.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FLUORINATED ETHERS  <b>(57) Abstract:</b>  A fluorinated ether which is the product of a fluorination reaction of an adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether. The fluorinated ethers are useful as inert fluids, especially as the working fluid of a heat pump.		

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/CB 84/00013 (SA 6462)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/05/84

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3816286	11/06/74	GB-A- 1430583	31/03/76
US-A- 2644823		None	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND NOT COMPLETELY SEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. Claim numbers searched incompletely: 1-9, 11, 12.

In the light of the general wording of claims 1-9, 11, 12 the search has been carried out with reference to the examples.

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

- 1-12 : Fluorinated ethers and process for their preparation
- 13-15 : Use of fluorinated ethers as working fluids and coolants, and heat pump containing fluorinated ethers
- 16 : Use of fluorinated ethers as fluid for vapour phase soldering
- 17 : Use of fluorinated ethers as lubricants

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers: 1-12.

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remarks on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

aryl, provided that both groups are not aryl. The preferred alkyl groups are methyl, ethyl and propyl but may also be butyl or larger groups.

Among the preferred hydrogen-containing ethers which  
5 may be used in accordance with the present invention are dimethyl ether, diethyl ether, dipropyl ether, tetrahydrofuran, dioxane, tetrahydropyran, trimethylene  
oxide, or ethylene glycol dimethyl ether.

The preferred fluoro-olefin is tetrafluoro-ethylene.  
10 Other fluoro-olefins which may be used are difluoroethylene, chlorotrifluoroethylene, perfluorocyclobutene, trifluoroethylene and hexafluoropropene. The mole ratio of the fluoro-olefin  
15 and the hydrogen-containing ether in the adduct may be from 6:1 to 1:1, but in certain instances may involve a larger amount of fluoro-olefin. For many working fluid applications, particularly for heat pump applications, it is preferred that the ratio of fluoro-olefin to the  
20 hydrogen-containing ether in the adduct is 2:1 or 1:1. The fluorinated ether according to the present invention may be one of the following compounds:

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FLUORINATED ETHERS

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This invention relates to certain fluorinated ethers and to the use of the fluorinated ethers in a number of diverse fields, especially as inert fluids, for example the working fluid of a heat pump.

10

The invention relates to novel fluorinated ethers which are the product of a fluorination reaction of an adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether. The fluorinated ether may be partially or fully fluorinated during the fluorination reaction. The hydrogen-containing ether is preferably of the formula  $R-O-R'$  wherein R and R' are hydrocarbon groups optionally substituted by chlorine or fluorine or together form a single hydrocarbon group and the total number of carbon atoms in the groups R and R' is preferably less than 10; specifically groups R and R' may be the same or different and maybe selected from alkyl, cycloalkyl, aralkyl and

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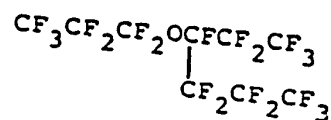
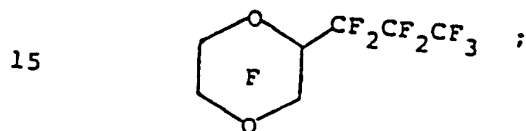
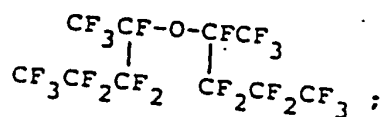
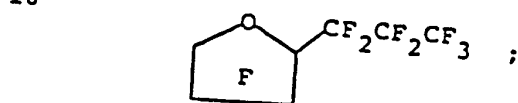
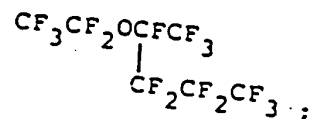
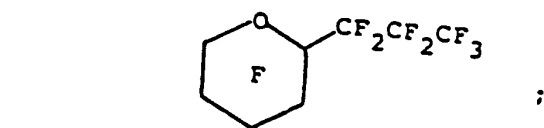
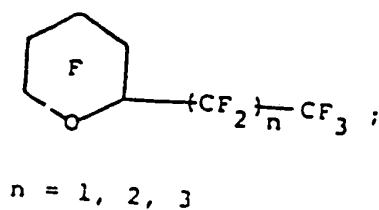
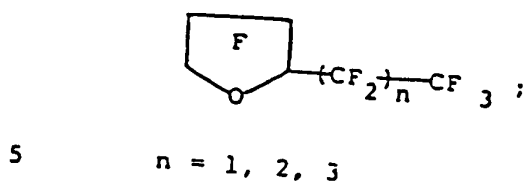




The present invention also includes a process for making fluorinated ethers as described above wherein the fluorination of the adduct is effected by the use of a high valency metal fluoride as a fluorinating agent at a temperature above 200°C. A fluorination procedure of this general kind is described in "Advances in Fluorine Chemistry" Vol 1. Butterworth, 1960 P 166. Cobalt trifluoride alone or in association with alkali or alkaline earth metal fluorides such as potassium fluoride or calcium fluoride are the preferred fluorinating agents. In the process of this invention, the fluorination is preferably effected in the temperature range 300°C to 600°C, eg. at temperatures between 400°C to 500°C.

The present invention is concerned with compounds which have good stability and by suitable selection compounds are provided for use as inert fluids and in particular for the working fluid of a heat pump. Furthermore, compounds may be selected which are particularly useful as heat pipe fluids, as coolants, as heat absorption media eg. for geothermal heat recovery, as lubricants, in vapour phase soldering, as solvents, especially in the separation of ethyl alcohol from aqueous mixtures, or as dielectrics. Several of these





20 In the above formulae the symbol F in the centre of the rings depicted indicates that all unmarked bonds are to fluorine atoms. This designation is used throughout the specification.

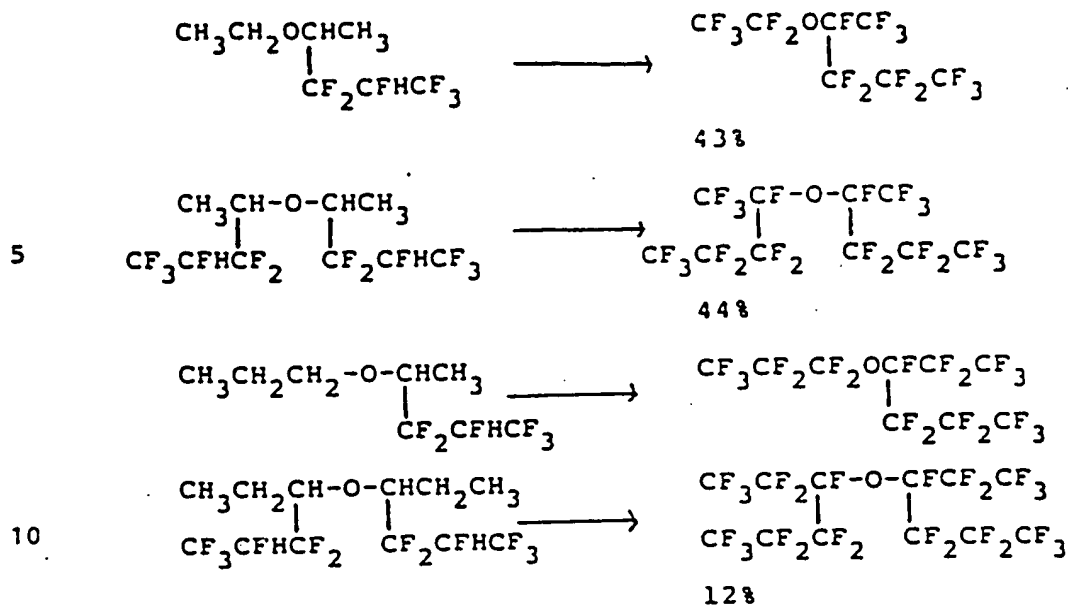
Fluorination with cobalt trifluoride is a technique well known in the art and is described in standard text books, for example R.D. Chambers "Fluorine in Organic Chemistry", see page 25. As is known, cobalt trifluoride  
5 can be re-generated by reacting elemental fluorine and the cobalt difluoride resulting from the organic fluorination reaction.

There is set out below a number of fluorination reactions in accordance with the present invention which  
10 have been carried out. All these fluorination reactions were effected, as indicated using cobalt trifluoride at 440°C.



uses require the fluorinated ether to have particularly high stability, which is a feature of the compounds of this invention. Furthermore, the use of partly fluorinated compounds as starting materials for the fluorination reaction in some cases substantially avoids, and not merely inhibits fragmentation of the adducts: additionally the fluorine containing adducts used in accordance with this invention permit controlled yields to be obtained with respect to various fluorinated ethers. It is known (see Journal of Fluorine Chemistry 1975 5 p 521 - Brandwood, Coe, Ely and Tatlow) that the usual experience with fluorination of hydrocarbon material containing no fluorine is the production of a complicated mixture of fluorinated and partially fluorinated products, including the products of fragmentation. In using the process of this invention employing cobalt trifluoride as a fluorinating agent at elevated temperatures complete fluorination can be effected if the temperature employed is of the order of 440°C, for the adducts exemplified in this specification. The selection of lower temperatures, but above 200°C, results in the production of partially fluorinated ethers.

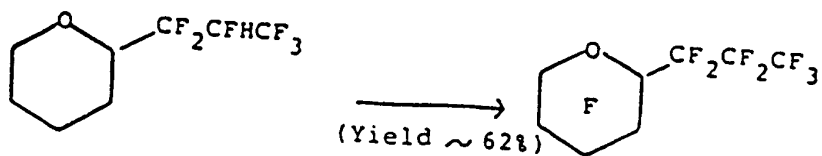




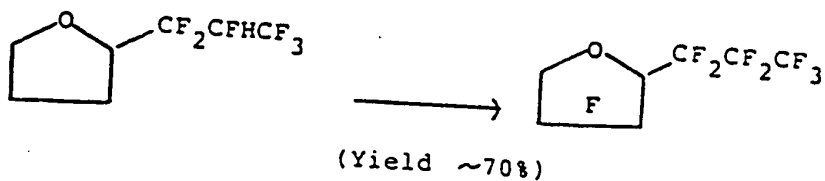
The use of the above-described cobalt trifluoride  
 technique the fluorination of an adduct in accordance  
 with the present invention enables the temperature  
 15 dependance of the fluorination technique using cobalt  
 trifluoride to be determined. The following Table I  
 gives the results of experiments conducted at various  
 temperatures using cobalt trifluoride and the adduct  
 20 2-(2-hydrohexafluoropropyl)oxolane. At temperature  
 below about 200°C virtually no fully fluorinated ether  
 is produced. On the other hand, at a temperature of  
 440°C very little product results other than an excellent  
 yield of the fully fluorinated adduct.

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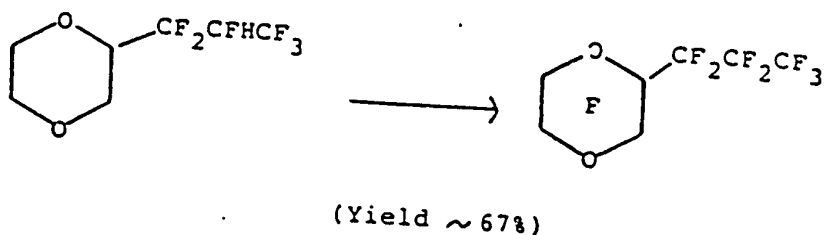




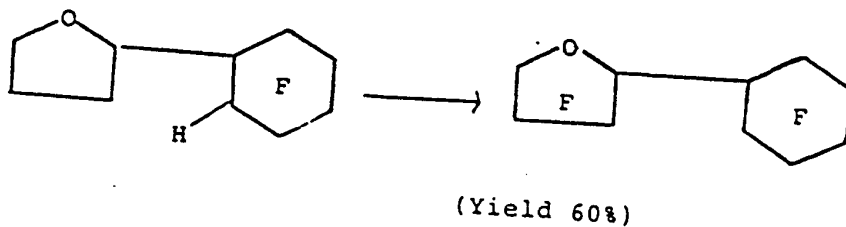
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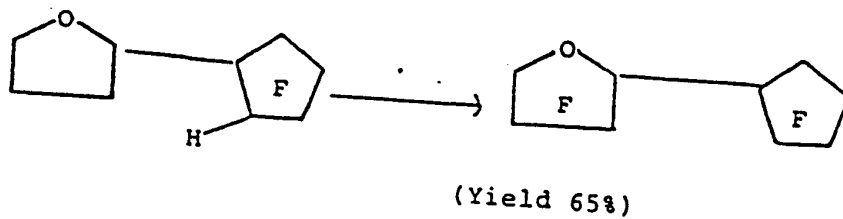
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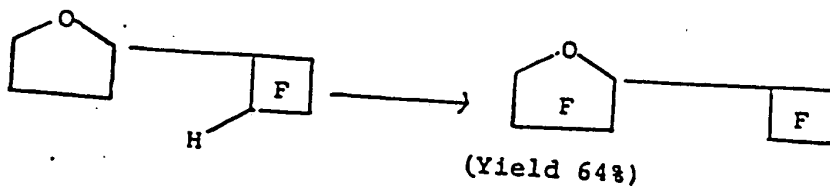
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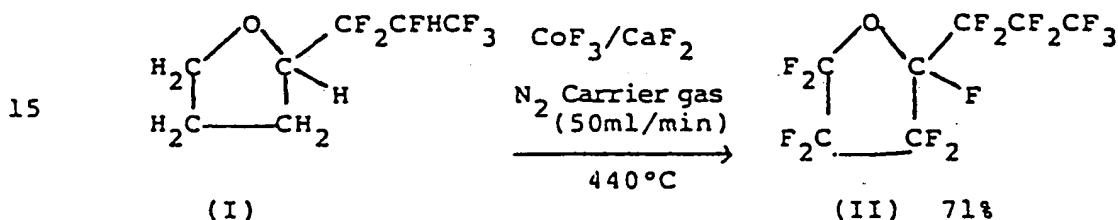
The following Examples illustrate in detail the preparation of fluorinated ethers in accordance with the present invention

5

### Example 1

#### Preparation of Perfluoro-2-Propyloxolane

10 2-(1,1,2,3,3,3,-hexafluoropropyl) oxolane was fluorinated with cobalt trifluoride/ $\text{CaF}_2$  to produce perfluoro-2-propyloxolane (II) in good yield.



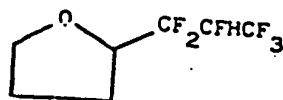
#### Experimental procedure

20

The fluorinating reagent (approx 330g) was generated by passing fluorine gas through a bed composed of 150g of cobalt difluoride and 150g of calcium difluoride until fluorine was detected at the bed outlet using

TABLE I

Temperature Dependence of the Cobalt Trifluoride  
Fluorination of 2-(2-hydrohexafluoropropyl) oxolane



$\xrightarrow{\text{N}_2 \text{ CARRIER GAS (50 ml/min)}}$

% Yield	Temperature(°C)	%C <sub>7</sub> F <sub>14</sub> O	%C <sub>7</sub> F <sub>13</sub> HO	%C <sub>7</sub> F <sub>12</sub> H <sub>2</sub> O	%C <sub>7</sub> F <sub>11</sub> H <sub>3</sub> O	%C <sub>7</sub> F <sub>10</sub> H <sub>4</sub> O and less- fluorinated derivatives
30% <sup>a</sup>	110	trace	1.3	3.7	23.3	71.1
49% <sup>b</sup>	180	trace	1.5	7.5	69.8	21.3
79% <sup>b</sup>	240	0.4	1.2	14.8	63.7	19.7
70% <sup>c</sup>	270	2.8	20.9	29.2	42.9	2.4
73% <sup>d</sup>	355	13.6	46.3	14.2	7.8	-
~70% <sup>e</sup>	440	~95%	~1%	-	-	-

a) Based on C<sub>7</sub>F<sub>6</sub>H<sub>8</sub>O  $\longrightarrow$  C<sub>7</sub>F<sub>10</sub>H<sub>4</sub>O

b) Based on C<sub>7</sub>F<sub>6</sub>H<sub>8</sub>O  $\longrightarrow$  C<sub>7</sub>F<sub>11</sub>H<sub>3</sub>O

c) Based on C<sub>7</sub>F<sub>6</sub>H<sub>8</sub>O  $\longrightarrow$  C<sub>7</sub>F<sub>12</sub>H<sub>2</sub>O

d) Based on C<sub>7</sub>F<sub>6</sub>H<sub>8</sub>O  $\longrightarrow$  C<sub>7</sub>F<sub>13</sub>HO

e) Based on C<sub>7</sub>F<sub>6</sub>H<sub>8</sub>O  $\longrightarrow$  C<sub>7</sub>F<sub>14</sub>O

Pure samples of the component fluorinated ethers of the reaction mixture can be isolated by conventional techniques. It is possible to "tailor" a particular fluorinated ether for a particular use. However, it is also possible to prepare mixtures of materials, appropriate to specific uses, by one of the three following methods:

- Mixing pure components,
- Partial fluorination of a single adduct,
- Fluorination of mixed adducts.





starch/iodide paper. Nitrogen gas was passed through the bed at 50ml/min for 30 minutes at the required temperature of 440°C. The oxolane compound I (1.93g, 8.7mmol) was added dropwise at a rate of about 1 ml in 10 minutes, and the products collected in a trap cooled by liquid air. The bed was flushed out with nitrogen for 15 minutes. The trap was warmed up to room temperature, anhydrous sodium carbonate was added to remove dissolved hydrogen fluoride, and the colourless liquid (2.27 g) separated. The liquid was distilled at atmospheric pressure to give perfluoro-2-propyl-oxolane, Bpt 79°C, with a yield of 71%.

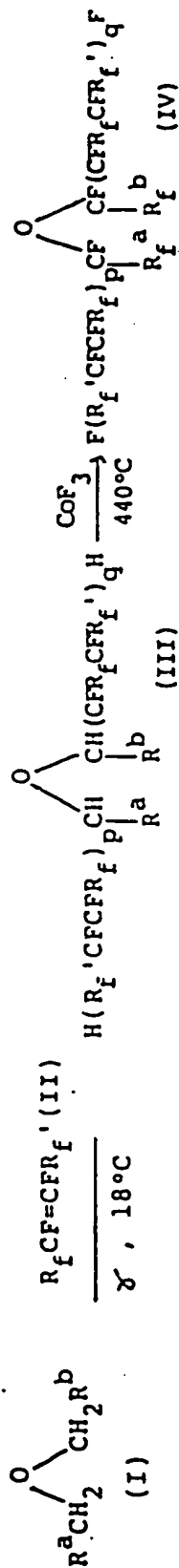


Example 2

The addition of a variety of ethers (I) to the  
5 fluoroalkenes (II) was carried out using  $\gamma$ -ray initiation  
of the reaction at ambient temperature to give the  
adduct (III), or a mixture of such adducts. The  
adduct(s) (III) were separated, purified and individually  
fluorinated using a cobalt trifluoride catalyst at a  
10 temperature of 440°C to give a variety of perfluoroethers  
(IV) and by-products (V). The results are summarised in  
Table II :



# ADDITION OF ETHERS TO PERFLUOROALKENES AND FLUORINATION TO PRODUCE PERFLUOROETHERS



where  $R_f^a$  and  $R_f^b$  represent the groups respectively with all the hydrogen atoms replaced by fluorine.

+ BY-PRODUCTS (v)





STARTING ETHER (I)	PERFLUORO- ALKENE (II)	ADDUCT (III)	% YIELD (III)	PERFLUORO- ETHER (IV)	% YIELD (IV)	Bpt (IV)	BY PRODUCTS (V)	% YIELD (V)	EXPERIMENT NUMBER
$(\text{CH}_3)_2\text{O}$	$\text{CF}_2=\text{CFCF}_3$	$p=1, q=0$	68	$p=1, q=0$	36	-	$\text{CF}_3(\text{CF}_2)_2\text{CF}_3$	44	1
		$p=1, q=0$	78	$p=1, q=0$	16			9	2
		$p=1, q=0$	74	Complex mixture of Products					3



TABLE II (Continued)

STARTING ETHER (I)	PERFLUORO- ALKENE (II)	ADDUCT (III)	% YIELD (II)	PERFLUORO- ETHER (IV)	% YIELD (IV)	Bpt (IV)	BY PRODUCTS (V)	% YIELD (V)	EXPERIMENT NUMBER
$(\text{CH}_3\text{CH}_2)_2\text{O}$	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	38	$\text{p=1, q=0}$	43	78	$\text{CF}_3(\text{CF}_2)_3\text{CF}_3$	10	4
		$\text{p=1, q=1}$	43	$\text{p=1, q=1}$	41	136	$\text{CF}_3(\text{CF}_2)_3\text{CF}_3$	9	
$(\text{CH}_3\text{CH}_2)_2\text{O}$	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	12	$\text{p=1, q=0}$	32	137	-	-	6
		$\text{p=1, q=1}$	28	$\text{p=1, q=1}$	12	162	$\text{CF}_3(\text{CF}_2)_4\text{CF}_3$	30	
$(\text{CH}_3\text{CH}_2)_2\text{O}$	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	16	$\text{p=1, q=0}$	18	149	$\text{CF}_3(\text{CF}_2)_5\text{CF}_3$	10	8
		$\text{p=1, q=1}$	28	-	-	-	$\text{CF}_3(\text{CF}_2)_5\text{CF}_3$	32	
$(\text{CH}_3\text{OCH}_2)_2$	$\text{CF}_2=\text{CFCF}_3$	$\text{CH}_3\text{OCHCH}_2\text{OCH}_3$   $\text{CF}_2\text{CFHCF}_3$	53	Complex mixture of Products					10
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	65	$\text{p=1, q=0}$	8	-	$\text{CF}_3(\text{CF}_2)_4\text{CF}_3$	10	11
							$\text{CF}_3(\text{CF}_2)_3\text{CF}_3$	3	

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TABLE II (Continued)




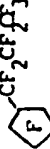

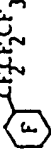
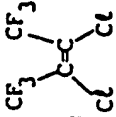
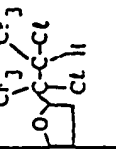
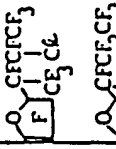
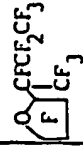


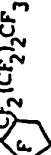


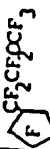



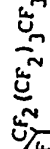
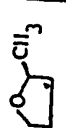

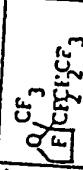
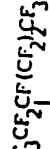

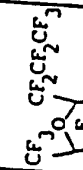

STARTING ETHER (I)	PERFLUORO-ALKENE (II)	ADDUCT (III)	YIELD (III)	PERFLUORO-ETHER (IV)	YIELD (IV)	IR (IV)	BY PRODUCTS (V)	YIELD (V)	EXPERIMENT NUMBER
	$\text{CF}_2=\text{CFCF}_3$	$p=1, q=0$	95	$p=1, q=0$	70	79	$\text{CF}_3(\text{CF}_2)_4\text{CF}_3$	5	12
	$\text{CF}_3\text{CF}=\text{CFCF}_3$	$p=1, q=0$	89	$p=1, q=0$	53	101	-	-	13
	$\text{CF}_2=\text{CFCl}$	$p=1, q=0, R_f' = \text{Cl}$	78	$p=1, q=0, R_f' = \text{Cl}$	45	82	-	-	14
		$p=1, q=0, R_f' = \text{F}$		$p=1, q=0, R_f' = \text{F}$	12	54			
		$p=1, q=0$	91	$p=1, q=0$	64	-	-	-	15
		$p=1, q=0$	83	$p=1, q=0$	65	117		11	16
		$p=1, q=0$	91	$p=1, q=0$	51	136		6	17
			89		16	-	-	-	18
					15	101	-	-	

TABLE II (Continued)

STARTING ETHER (I)	PERFLUORO-ALKYNE (II)	ADDUCT (III)	PERFLUORO-ETHER (IV)	YIELD (IV) %	Bopt (IV)	BY PRODUCTS (V)	YIELD (V) %	EXPERIMENT NUMBER
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	$\text{p=1, q=0}$	62	-	-	-	19
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	$\text{p=1, q=0}$	31	134		20	20
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	$\text{p=1, q=0}$	68	90	-	-	21
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	$\text{p=1, q=0}$	17	125		8	22
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	$\text{p=1, q=0}$	45	124		10	23
	$\text{CF}_2=\text{CFCF}_3$	$\text{p=1, q=0}$	$\text{p=1, q=0}$	20	158		22	24
	$\text{CF}_2=\text{CFCF}_3$			18	101		10	25
				25	94			

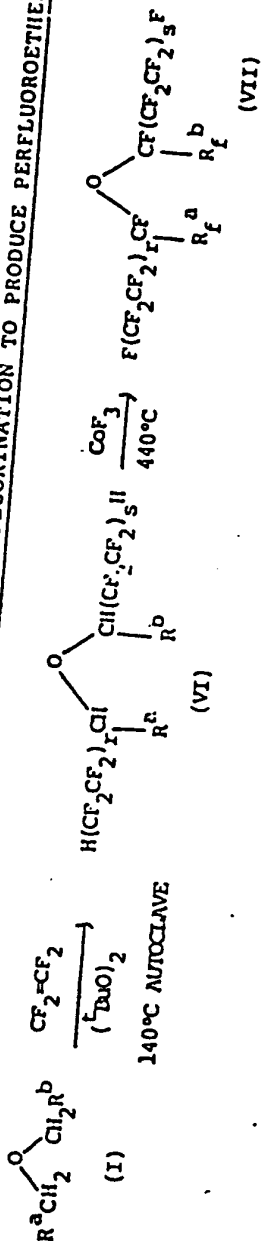
Example 3

The addition of a variety of ethers (I) to  
5 tetrafluoroethene ( $\text{CF}_2=\text{CF}_2$ ) was carried out using a  
tertiary butyl peroxide catalyst at a temperature of  $140^\circ\text{C}$   
in an autoclave. Each ether (I) gave a mixture of  
adducts (VI) which were separated and fluorinated  
individually using a cobalt trifluoride catalyst at a  
10 temperature of  $440^\circ\text{C}$  to give the perfluoroethers (VII).  
The results are summarised in Table III:



TABLE III

ADDITION OF ETHERS TO TETRAFLUOROETHENE AND FLUORINATION TO PRODUCE PERFLUOROETHERS



where  $R_f^a$  and  $R_f^b$  represent the groups  $R^a$  and  $R^b$  respectively with all the hydrogen atoms replaced by fluorine.



STARTING ETHER (I)	ADDUCT (VI)	% YIELD (VI)	PERFLUOROETHER (VII)	% YIELD (VII)	Dpt (°C) (VII)	EXPERIMENT NUMBER
	$r=1, s=0$	61	$r=1, s=0$	65	54	1
	$r+s=2$	30	$r=1, s=1$	65-70	93	2
	$r+s=3$	8	$r=2, s=0$		-	3
	$r+s=4$	0.8	$r=2, s=1$ $r=3, s=0$ $r=3, s=1$ $r=4, s=0$	61 55	132 141 - -	4



TABLE III (Continued)

STARTING ETHER (I)	ADDUCT (VI)	% YIELD (VI)	PERFLUOROETHER (VII)	% YIELD (VII)	Bpt (°C) (VII)	EXPERIMENT NUMBER
	r=1, s=0	57	r=1, s=0	33	65	5
	r + s = 2	30	r=1, s=1 r=2, s=0	34	103 110	6
	r + s = 3	11	r=2, s=1 r=3, s=0	38	141 150	7
	r + s = 4	2	r=3, s=1 r=4, s=0	35	174 180	8
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O	r=1, s=0	51	r=1, s=0	23	56	9
	r + s = 2	37	r + s = 2	31	98	10
	r + s = 3	10	r + s = 3	35	-	11
	r + s = 4	2	r + s = 4	35	-	12

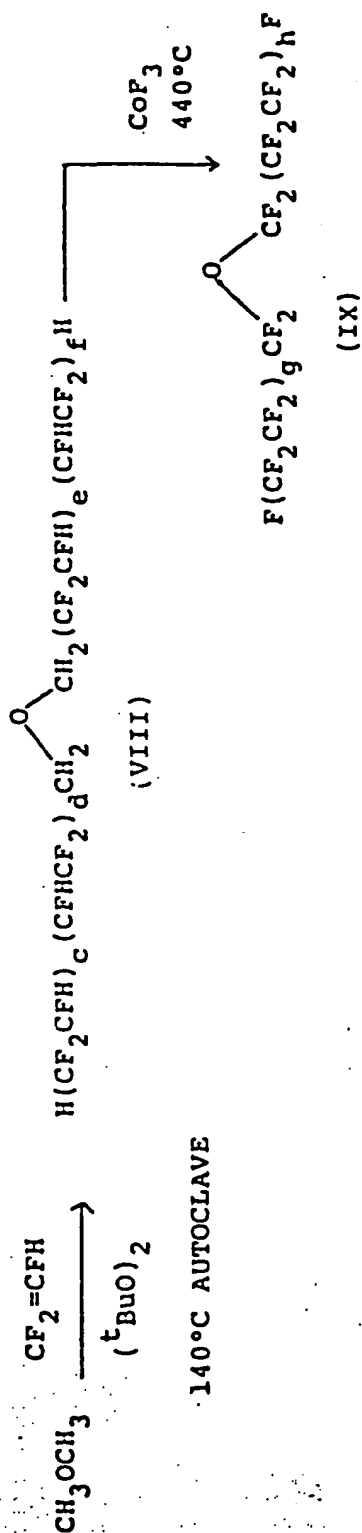
Example 4

Dimethyl ether was added to trifluoroethene by a  
5 free-radical reaction using a tertiary butyl peroxide  
catalyst at a temperature of 140°C in an autoclave. The  
product mixture was separated into the adduct isomer  
mixtures (VIII) which were fluorinated using a cobalt  
trifluoride catalyst at a temperature of 440°C to give  
10 the perfluoroethers (IX) the by-products (X). The  
results are summarised in Table (IV):



TABLE IV

# ADDITION OF DIMETHYLETHER TO TRIFLUOROETHENE AND FLUORINATION TO PRODUCE PERFLUOROETHERS



+ BY-PRODUCTS (X)

ADDUCT (VIII)	% YIELD (VIII)	PERFLUOROETHER (IX)	% YIELD (IX)	Bpt (IX) (°C)	BY-PRODUCTS (X)	% YIELD (X)	EXPERIMENTAL NUMBER
c+d+e+f = 1	62	UNIDENTIFIED MIXTURE OF PERFLUORINATED PRODUCTS					1
c+d+e+f = 2	30		14	62	-	-	2
c=d=e=f = 3	6		7 3	106 -	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CF <sub>3</sub> CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> CF <sub>3</sub>	29 12	3

It is to be understood that in making the novel fluorinated ethers according to the present invention other techniques for fluorinating the adducts may be employed, for example elemental fluorine or  $\text{ClF}_3$  or electrochemical fluorination may be employed.

In many working fluid situations the working fluid is exposed to cyclic temperature changes, and the fluorinated ethers according to this invention provide compounds or mixes of compounds which are suitable for this purpose. The fluorinated ethers may be employed in an apparatus in which there is transfer of heat from a higher to a lower temperature, or alternatively in an apparatus where there is transfer of heat from a lower to a higher temperature. Furthermore, it is to be noted that the fluorinated ethers may be used in apparatus in which there is a change from a liquid to a vapour state, and back to the liquid state, such as is the case with the heat pump. A particular use where a change of state is involved is in using these working fluids in a refrigerator: another use is in the transfer of heat in chemical reactors and the like. One particular situation where the fluorinated ethers of this invention may be used with advantage is in the generation of power, for



example Organic Rankine Cycle power generation or the abstraction of heat from geothermal sources, including the conversion of geothermal energy to work.

The compounds or mixtures of compounds according to  
5 the invention for use as the working fluid in a heat pump may be chosen so as to provide the desired critical temperature and boiling point. Other factors are relevant, but these are the prime ones. The critical temperature and boiling point desired will depend upon  
10 the condensing and evaporating temperatures used in the heat pump.

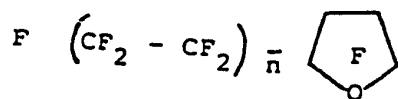
A suitable substance for use as a working fluid in a heat pump condensing at  $T_C$  and evaporating at  $T_E$  would have a critical temperature substantially higher than  $T_C$   
15 and a normal boiling point substantially lower than  $T_E$ . Thus for example, if  $T_C = 150^\circ\text{C}$  and  $T_E = 100^\circ\text{C}$ , a possible working fluid would be 1,1,1,2,3,3-hexafluoro butyl methyl ether which has a critical temperature of  $236^\circ\text{C}$  and a normal boiling point of  $87^\circ\text{C}$ , or  
20 perfluoro-2-propyloxolane which has a critical temperature of  $206^\circ\text{C}$  and a normal boiling point of  $79^\circ\text{C}$ .

Adducts formed by reacting tetrafluoroethylene



( $\text{CF}_2 = \text{CF}_2$ ) with hydrogen containing, eg. hydrocarbon, ethers are formed as mixtures of products. The reaction tends to produce telomers of the type  $\text{H} (\text{CF}_2 - \text{CF}_2)_n - \text{R} \text{O} \text{R}'$  where  $n$  may be from 1 to well above 8.

- 5 Fluorination of these telomer mixtures can produce mixtures of compounds according to the invention having boiling points, critical temperatures and other properties suiting them for particular uses. For instance, when tetrafluoroethylene is reacted to add to  
 10 tetrahydrofuran the products after fluorination have the formula:



- 15 Products are obtained which are useful, for example, as follows:

- |                            |                                |
|----------------------------|--------------------------------|
| for low values of $n$      | - working fluids and coolants, |
| intermediate values of $n$ | - fluids for vapour phase      |
|                            | soldering, and                 |
| 20 higher values of $n$    | - lubricants                   |



## CLAIMS:

1. A fluorinated ether which is the product of a  
5 fluorination reaction of an adduct formed by the  
free-radical addition of a fluoro-olefin and a  
hydrogen-containing ether.
2. An ether as claimed in claim 1 which is fully  
10 fluorinated during the said fluorination reaction.
3. An ether as claimed in claim 1 or claim 2  
wherein the hydrogen-containing ether is of the formula  
R-O-R' wherein R and R' are hydrocarbon groups or  
15 together form a single hydrocarbon group and the total  
number of carbon atoms in the hydrocarbon groups R and R'  
is up to 10.
4. An ether is claimed in claim 3 wherein the  
20 groups R and R' are the same or different and are methyl,  
ethyl, propyl or butyl groups.
5. An ether as claimed in claim 3 wherein the  
groups R and R' contain halogen.



6. An ether as claimed in any one of the preceding claims wherein the fluoro-olefin is tetrafluoro-ethylene or hexafluoropropene.

5 7. An ether is claimed in any one of the preceding claims wherein the hydrogen-containing ether used in forming the adduct is dimethyl ether, diethyl ether, dipropyl ether, tetrahydrofuran, dioxane, tetrahydropyran, trimethylene oxide, or ethylene glycol  
10 dimethyl ether.

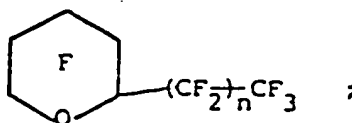
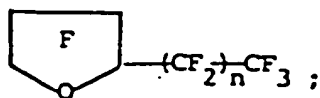
8. An ether as claimed in any one of the preceding claims wherein the ratio of the fluoro-olefin to the hydrogen-containing ether in the adduct is 6:1 to 1:1.  
15

9. An ether as claimed in any one of the preceding claims wherein the ratio of the fluoro-olefin to the hydrogen-containing ether in the adduct is 2:1 or 1:1.

20 10. An ether as claimed in claim 1 which is the product of a fluorination reaction and is one of the following:



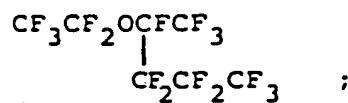
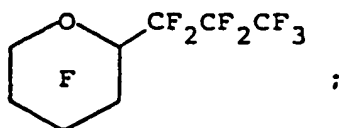




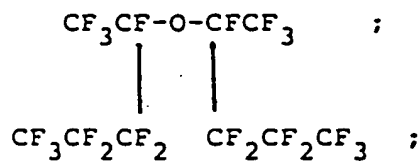
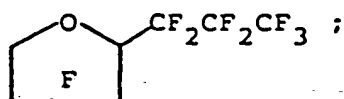
$n = 1, 2, 3$

$n = 1, 2, 3$

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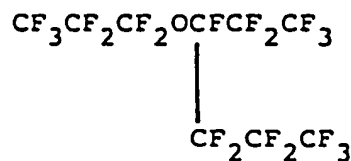
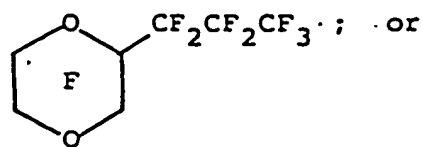


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11. A process for the preparation of an ether as claimed in any one of the preceding claims wherein the fluorination of the adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether is effected by the use of cobalt trifluoride as a fluorinating agent at a temperature of above 200°C.

12. A process is claimed in claim 11 wherein the temperature employed is in the range of from 400°C to 450°C.

13. The use as a working fluid of a fluorinated ether as claimed in any one of the claims 1 to 10.

14. A heat pump wherein the working fluid employed is a fluorinated ether as claimed in any one of claims 1 to 10.

15. The use as a coolant of a compound as claimed in claim 1 and of the formula  $R' O R - (CF_2 - CF_2)_n F$  wherein  $R' O R-$  is the fluorinated residue of a hydrogen containing ether and  $n$  is from 2 to 4.



16. The use as a fluid for vapour phase soldering of  
a compound as claimed in claim 1 and of the formula  $R' O R - (CF_2 - CF_2)_n F$  wherein  $R' O R -$  is the fluorinated  
residue of a hydrogen containing ether and  $n$  is from 4 to  
5 7.

17. The use as a lubricant of a compound as claimed  
in claim 1 and of the formula  $R' O R - (CF_2 - CF_2)_n F$   
wherein  $R' O R -$  is the fluorinated residue of a hydrogen  
10 containing ether and  $n$  is 8 or more.



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 84/00013

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>3</sup> : C 07 D 307/18; 309/08; 319/12; C 07 C 43/12; 41/22; F 25 B 29/00; B 23 K 28/00; C 10 M 3/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC <sup>3</sup>	C 07 D 307/00; C 07 D 309/00; C 07 D 319/00; C 07 C 43/00; C 07 C 41/00	
Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> **		
Category *	Citation of Document, <sup>13</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	Chemical Abstracts, vol. 94, no. 5, 2 February 1981 (Columbus, Ohio, US) R.D. Chambers et al.: "Free radical chemistry. Part 2. Additions of dimethyl ether to F-cycloalkenes", see page 490, abstract no. 29806u, J. Fluorine Chem. 1980, 16(4), 351-64 (Eng.)	1, 3, 4, 7-9, 11, 12
Y	---	6, 7
Y	US, A, 3816286 (R.N. HASZELDINE) 11 June 1974 see examples V, VI, XXVII	6, 7
X	US, A, 2644823 (E.A. KAUCK) 7 July 1953 see the entire document	10
<p>* Special categories of cited documents: <sup>16</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>1</sup>		Date of Mailing of this International Search Report <sup>1</sup>
12th April 1984		29 JUN 1984
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
EUROPEAN PATENT OFFICE		G.L.M. Kruseenberg